Preboiled and cooled 20 ozs. of distilled water, and divided into two exactly equal portions. Took two portions of 50 grs. each of partly dehydrated sodic carbonate; heated one portion to 180° F. for fifteen minutes until it ceased to evolve moisture (it lost 12·4 grs.), and cooled it. Dissolved the two separate portions of salt in the separate quantities of water, and tested the solutions against each other in the two apparatuses. No difference of strength of current occurred at any temperature up to that of 180° F.

In another experiment of this kind, 200 grs. of ammonia alum were divided and treated as above. The solution of the non-preheated portion gave the strongest current; deflection ·75° at 180° F.

Remarks.—The conclusion I draw from these last two experiments and results, combined with those of the previous ones, is that preheating the salt either before or after solution usually weakens the current, both in thermo-electropositive and in thermo-electronegative liquids.

In the several classes of cases described in this paper, it is evident that the currents are not due to chemical action, but to heat acting upon and altering particular molecular structures, and that the difference of electromotive power in different liquids is not due to differences of chemical action, but probably to differences of molecular arrangement of the solutions. Also that in the class of experiments where the liquids compared had the same chemical composition, but had been differently treated, the differences of molecular arrangement were less, and the currents obtained were consequently more feeble. A difference of strength of current caused by repetition of experiments, or by continuance of heat, also renders manifest the change of molecular arrangement; and the above method may be employed for detecting molecular differences in conducting liquids having the same chemical composition.

In the class of cases in which the differences of molecular arrangement were the least, and the currents the most feeble, the direction of the currents was the most uniform. This is in accordance with the common truth in science that the smallest phenomena are the most constant.

II. " Quantitative Spectroscopic Experiments." By Professor G. D. LIVEING, M.A., F.R.S., and Professor JAMES DEWAR, M.A., F.R.S. Received November 27, 1879.

The well-known expansion of the lines of sodium and other metals, when increased quantities of the metals are introduced into the flame or arc, seems to afford a means of attaining a quantitative spectrum analysis in certain cases, if the relations between the width of

the lines and the thickness, density, and temperature of the vapours could be determined. We had such a determination in view during our experiments on the reversal of the lines of metallic vapours heated in iron tubes, and have since made a good many experiments expressly for the purpose. We have not yet overcome all the difficulties attending these experiments; nevertheless, some results, definite and interesting, have been reached, which we now communicate to the Society.

The first experiments were made with wrought iron bottles, of the form shown in the accompanying figure. To prevent the diffusion of carbonic oxide from the fire we found it essential to have the wide
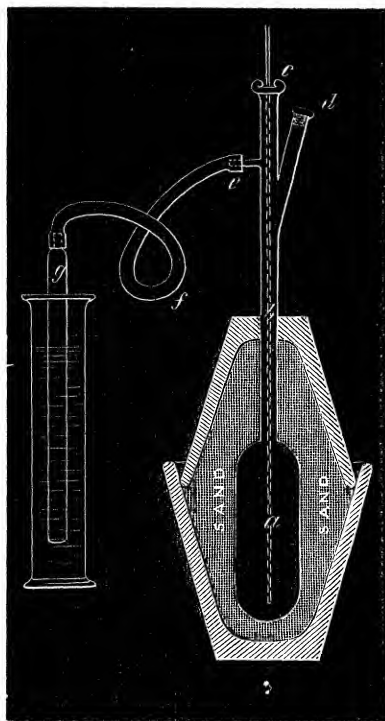
part, *a*, and part of the tube, *b*, coated with borax. The bottle was then packed in sand in two crucibles, one of them inverted, and heated in a small furnace fed with gas retort carbon. The bottle was previously treated with fused caustic potash at a red heat, and washed with acid. Any oxide remaining in the bottle was reduced by a current of hydrogen introduced by the side tube *e*, and forced to pass to the bottom by allowing it no exit except by a narrow tube passed through the opening *c* and reaching nearly to the bottom of the bottle, as

shown by the dotted lines. The hydrogen was then replaced by nitrogen, the narrow tube removed, c closed by a glass plate through which the spectrum was viewed, and the side tube e connected by a thick rubber tube with a glass tube for collecting the gas driven out by the metallic vapour, or with a manometer formed of an inverted burette dipping into a vessel of water. The sodium, weighed in dry carbonic acid gas, was introduced in little iron cups about the size of gun caps through the oblique side tube d, and the orifice instantly closed with a rubber stopper, for the purpose of measuring the gas expelled as the sodium evaporated. This orifice was fitted with a screw cap, for use when the pressure of the gas in the bottle was to be varied.

Attempts to measure the temperature of our furnace were not very successful. Observations of temperature depending on the electromotive force of a thermo-electric junction of platinum and palladium, which had been carefully calibrated in boiling mercury, boiling cadmium, and boiling zinc, failed at the temperature at which our experiments were made from the fusion of the palladium. This indicates, from Violle's experiments, that the temperature of the furnace was about 1,500° C.

The bottles, however carefully cleaned, were never quite free from sodium, so that on observing, at first, the spectrum emitted by the hot bottom of the bottle, the D absorption was seen as two fine lines.

On introducing a fragment of sodium (·015 or ·020 grm.) the following phenomena were observed with the spectroscope. First D appeared as a narrow *bright* band, considerably brighter than the general spectrum of the bottle, with the fine dark pair of lines quite unexpanded in its midst; this bright band rapidly expanded, becoming fainter and more diffuse as it expanded, was visible to a width equal to fourteen or sixteen times the distance of the D lines from each other, and then died away entirely, leaving the fine dark lines much as they were at first. The addition of several pieces of sodium in succession produced a repetition of the same phenomena, the D absorption lines being but very little wider after the introduction of sodium enough to fill the bottle with its vapour.

Larger pieces of sodium produced an increased width of expansion of the bright band; but from the very diffuse character of the edges of the band and from its being seen against a background only a little less bright, it was not possible to get any exact measures of the widths to which the bands expanded.

On observing the gas expelled from the bottle, it was found that the expansion of the bright band was synchronous with the expulsion of gas, and ceased when gas ceased to come out; that is to say, it was synchronous with the expansion of the sodium vapour within the bottle. It was found, however, that when the gas ceased to be ex-

pelled from the bottle, it almost immediately began to be sucked back, and that nearly, if not quite, as rapidly as it had been expelled, until not only the whole gas expelled was drawn in again, but generally a small quantity of nitrogen in addition. In a few seconds, not only had the sodium vapour ceased to have any sensible tension, but a portion of the nitrogen (2 to 3 cub. centims.) had been absorbed. There was no absorption of nitrogen before the sodium was put in, and when the equilibrium had been attained, which was always in less than a minute, there was no absorption afterwards.

These phenomena seemed to indicate, (1), either that the temperature of the sodium vapour was higher than that of the iron, or that the emissive power of sodium vapour for light of the wave-length of D was greater than that of iron at the temperature of the furnace; (2), that the width of the bright D line, or band, increased with the depth of the stratum of sodium when the density was not increased, inasmuch as the pressure to which the sodium vapour was subject was always the same, and the only, or the principal, change during the expansion of the sodium vapour in the bottle was in the thickness of the layer of vapour; (3), that iron either has the power of forming a compound with sodium, which is very stable at the temperature of the furnace, or else it has a power of transmitting sodium vapour analogous to that which platinum has in regard to hydrogen. This last supposition seems to be negatived by the fact that we found that out of ·220 grm. of sodium put into the bottle in a series of experiments on one occasion, ·198 grm. was afterwards extracted when the bottle was cold by washing it out with hydrochloric acid. The effect was not due to the nitrogen, since the sodium appeared to be taken up in the same way when carbonic oxide was substituted for nitrogen.

This behaviour of iron towards sodium explains a phenomenon which had puzzled us when operating before with iron tubes, viz., that it required a very large quantity of sodium, many times the normal amount, to fill one of the tubes with sodium vapour. It also seems to explain the fact observed by Mr. Lockyer (Proc. Roy. Soc., vol. xxii, p. 371), that sodium heated in a long iron tube gives the D absorption line " no thicker than when seen under similar conditions in a test tube."

We came, of course, to the conclusion that it was useless to pursue the investigation of the quantitative measure of sodium vapour by experiments in iron vessels; and we had a stout platinum tube made, half an inch in diameter and 23 inches long, connected by a union joint with an iron tube with fittings similar to those of the top of the iron bottles before described; and also a bottle similar to the iron bottles, but entirely of platinum. When used, the tube was packed with magnesia inside a wider porcelain tube, and the bottle was packed with lime in blacklead crucibles.

For convenience in introducing the sodium, a fine platinum tube, about 1 millim. in diameter, was filled with sodium by sucking up the melted metal, and different lengths of this tube were cut off as required, wrapped at once in thin platinum foil, and dropped into the heated vessel. Amalgams containing various percentages of sodium were also employed. In the case of amalgams containing 1 per cent. and upwards the pieces were weighed; those containing less than 1 per cent. were measured by a very fine pipette. In all cases the amalgam was introduced into the hot vessel wrapped in platinum foil.

For varying the pressure within the vessels, and so by compression or expansion varying the density and thickness of the stratum of metallic vapour under observation, an ordinary compressing and exhausting syringe, connected with a gauge, was used. With the bottle we could not venture to reduce the pressure below that of the atmosphere, lest the softened platinum should collapse; but in the case of the tube the pressure could be reduced to one-fourth of an atmosphere. Into both vessels we have pumped nitrogen until the pressure reached three atmospheres.

Whenever it was desired to empty the vessel of sodium, in order to begin a fresh series of experiments without the necessity of cooling the vessel, the sodium (or sodium and mercury) vapours were blown out by a current of hydrogen passed down to the bottom of the vessel in the mode already described, and when the metallic vapours were sufficiently expelled, the hydrogen was replaced by nitrogen. In this way, though the last traces of sodium were never expelled, the D absorption could be reduced to two narrow lines.

On introducing a fragment of sodium into the hot vessel, when free, or nearly so, from sodium to begin with, the *bright* yellow band rapidly expanding and becoming fainter and more diffuse, and finally dying away, was seen as in the iron bottles; but instead of the D absorption remaining narrow as it had been before, it began to increase in width as the bright band died away, and soon attained a maximum width, and remained steadily at that width—a width several times that of the distance between the D lines, but much less than that of the bright band at its widest. A second piece of sodium thrown in produced a repetition of the same phenomena, except that the bright band was obscured by the absorption of the layer of sodium vapour first introduced, and only seen when it expanded beyond the absorption band. More pieces of sodium produced like effects; the absorption band gradually widening as more sodium was put in, until the channelled spectrum began to appear.

The effects of compressing the vapour were very remarkable. As the pressure increased the channelled spectrum speedily disappeared, then the diffuse edges of the D band contracted, the band itself likewise contracting until it became a very fine pair of lines,

or if the amount of sodium present was not too much, D came
out bright. On letting off the pressure, the phenomena recurred
in the reverse order, and the whole could be repeated several
times. After compression as long as the pressure was sustained the D
absorption remained permanently narrowed, but did not continue
bright. When there was only a very little sodium in the platinum
tube and the pressure diminished, the D band was seen to expand and
become diffuse, contracting again as the pressure was restored, but
not generally contracting to quite its former width or sharpness.

We used sometimes amalgams of sodium in order to have a very
dense gas to retard diffusion, and for the purpose of getting various
quantities of sodium diffused through equal spaces. With these
amalgams the general course of the phenomena was much the same as
with the metal alone, except that we could not by compression to
three atmospheres make the D lines show out so bright as with
sodium alone, although the absorption was reduced to extremely
narrow dimensions.

One set of experiments was made with a series of amalgams con-
taining decreasing percentages, all less than 1 per cent., of sodium,
equal quantities of each were put into the hot tube in succession, the
vapour of each being blown out before the next was put in. The
thickness of the layers observed was thus very nearly constant, but the
density of the sodium vapour variable. It was calculated that the
mercury vapour would, at the temperature of the tube, fill a height
of about 20 centims. The D absorption was very broad, with
wide diffuse edges, with an amalgam of $\frac{1}{2}$ per cent., and did not
sensibly diminish in width until the percentage of sodium was re-
duced to $\frac{1}{8}$.

The results of the foregoing experiments may have been complicated
by the sodium vapour which diffused into the cool part of the vessel.
We have attempted to overcome this complication by passing down
into the bottle, when full, or nearly full, of sodium vapour, a platinum
tube closed at the top with a glass plate, and filled with nitrogen, and
observing the absorption through this tube. The nitrogen in the tube
prevents for a short time the entry of the sodium vapour into the
tube, and so by passing the tube to different depths, the thickness of
the layer of sodium through which the observations were made could
be varied. It was found in this way that a layer of sodium vapour,
about 4 centims. thick at the atmospheric pressure at the tem-
perature of our furnace, gave the D absorption sharp and very narrow,
but as the sodium diffused into the tube the absorption extended until
it produced a broad band with diffuse edges. Without a long process
of washing, it is impossible to clear the tube of sodium, so that the
repetition of observations in this way is a very tedious business. We
are looking for some transparent substance which will stand the high

temperature and the action of sodium, wherewith to close the lower end of our tube of inspection. We have tried a plate of colourless sapphire, but it very soon became too opaque for further use. Perhaps fused alumina may do better.

A few experiments made in a similar way with thallium in iron bottles, showed on the whole similar results. No bright green line was seen on dropping in a piece of thallium, but it was not until after the lapse of some seconds that the absorption line was apparent. It was faint at first, gradually deepening, and soon attaining a maximum of intensity, when it was remarkably stationary for a long time. More pieces of thallium introduced successively produced a small but perceptible widening of the absorption band and a diminution of the sharpness of its edges.

The foregoing account gives the general course of the phenomena, and it seems useless at present to describe further details, because the quantitative results which we hoped to give are for the time in abeyance until we can ascertain more correctly the temperature of our furnace and the thickness of the layer of vapour observed. This requires an accurate knowledge of the density of the vapour, which could not be satisfactorily deduced from the experiments made with iron bottles, as they did not accord well and were complicated by the action of iron on sodium above described. The platinum vessels stand but few experiments without repair, which causes considerable delay ; and the above-mentioned results have necessitated the expensive operation of the reconstruction of some five platinum bottles.

The phenomena attending the compression of the vapours, as well as those of the amalgams of varying percentages, seem to indicate that the width of the D absorption is dependent on the thickness and temperature of the absorbent vapour rather than on the whole quantity of sodium present in it. Very minute quantities diffused into the cool part of the tube appear to give a broad diffuse absorption, while a layer of denser vapour of small thickness in the hottest part of the vessel gives but a very narrow absorption. This may, however, be due to the variation of temperature.

The phenomena of the bright D band seen on compressing the vapour is due to the elevation of temperature consequent on compression. This elevation, we have calculated, for a *sudden* compression to half the original volume, will amount in the case of sodium vapour, if the ratio of the specific heat at constant pressure to that at constant volume be taken as 1·14, to about one-third of the original temperature, whatever that temperature be ; so that, allowing for loss during slower compression, the temperature of the vapour in our bottles will have nearly reached 2,000°. In the case of the amalgams the main portion of the gas being mercury vapour, the effect of compression to a like amount will increase the temperature by nearly two-

thirds, in consequence of the ratio of the specific heat at constant pressure to that at constant volume being now 1·66. It is not so easy to explain why the bright band should appear while the sodium is evaporating, when a depression of temperature should ensue. The depression of temperature will, however, affect the hot bottom of the vessel, and so it and the lowest layer of sodium vapour may be relatively cooler than the layers above. Professor Stokes has suggested another cause which may intensify the effect, depending on the fact that the radiation from the sides of the vessel is partly reflective, partly emissive, while that from the sodium is almost wholly emissive. The bottom of the vessel will be somewhat diminished in brightness by the opening opposite giving no radiation to be reflected by it, while the temperature of the sodium being well sustained by the radiation of the sides, the want of radiation from the opening will not make any sensible change in its emission. Whatever explanation be given of the cause, the fact of the gradual expansion of the bright band as the sodium evaporates bears out the supposition that an increased thickness of sodium vapour, with little or no change of density, produces a wider line.

The very minute quantity of sodium required to produce a wide absorption was shown in the experiments with the amalgams. In one of these ·042 grm. of an amalgam containing only $\frac{1}{8}$ per cent. of sodium was introduced into the platinum tube. That quantity of mercury would at 1,500° C., which was about the temperature of the furnace, fill about 25 cub. centims., occupying a depth of about 20 centims. of the tube. In this volume there was only about ·00005 grm. of sodium, yet the D absorption band was at least twice as wide as the space between the two D lines.

The quantity of sodium requisite to give the channelled spectrum also appears to be very small. Between 4 and 5 mgrms. put into the platinum bottle, whether alone or as an amalgam, usually gave the channelled spectrum; sometimes it was seen with even less than 4 mgrms. Now the wide part of the bottle held some 200 cub. centims., so that the quantity of sodium diffused through this space and up into the tube would give a vapour of very small density indeed. The complete disappearance of the channellings as soon as the vapours were a little compressed, so as to be driven down into the hot part of the bottle, seems to indicate that the channellings were due to comparatively cool vapour in the upper part of the vessel.

The facility with which very high temperatures can be obtained by sudden compression, naturally suggests a repetition of our experiments with the electric arc in lime crucibles, under circumstances in which a pressure of a few atmospheres can be suddenly applied; and this we hope to carry out.